162-89 AU 133 49105

WO 9105909
MAY 1991

ELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification [5] **:** D21C 9/14, 9/147

A1

(11) International Publication Number: **WO 91/05909**

(43) International Publication Date: 2 May 1991 (02.05.91)

(21) International Application Number: PCT/US90/05825

(22) International Filing Date: 17 October 1990 (17.10.90)

(30) Priority data:
424,347 19 October 1989 (19.10.89) US

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(81) Designated States: AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH (European patent), CM (OAPI patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL (European patent), NO, RO, SD, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent).

Published
With international search report.
With amended claims

(54) Title: HIGH EFFICIENCY CHLORINE DIOXIDE PULP BLEACHING PROCESS

(57) Abstract

A high-efficiency wood pulp bleaching process to produce wood pulps with higher brightness at equal chlorine dioxide usage or of equal brightness at significantly reduced chlorine dioxide usage. The process comprises reacting the chlorine dioxide with wood pulp at a pH of about 5-10 for about 5-40 minutes and then acidifying the mixture to a pH of about 1.9-4.2. The mixture is then allowed to react for about 2 or more hours to complete the two-step high/low pH bleaching process.

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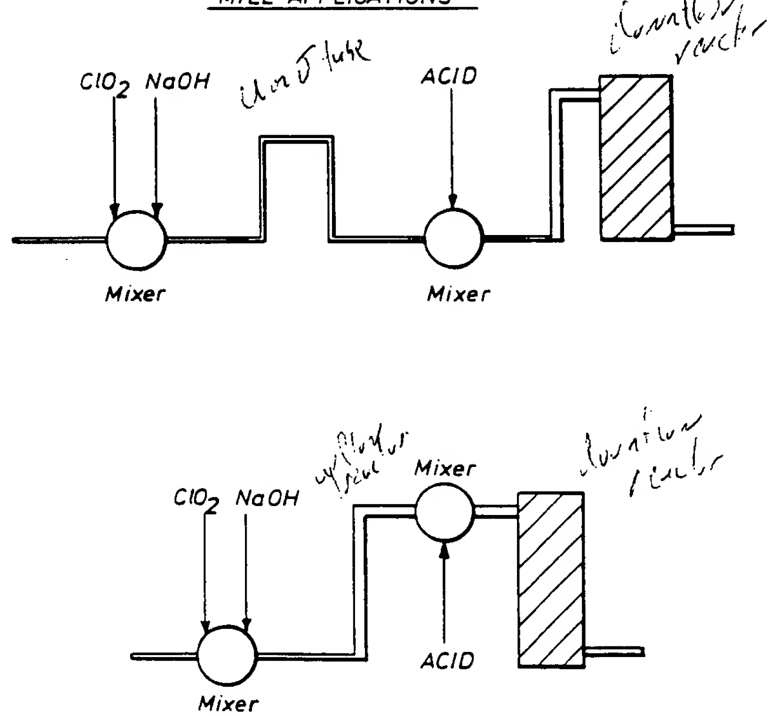

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Description

HIGH EFFICIENCY CHLORINE DIOXIDE PULP BLEACHING PROCESS

Technical Field

The present invention relates to the bleaching of pulp and more particularly to an improved process for bleaching wood pulp with chlorine dioxide in a manner whereby the wood pulp is subjected to a 2-step high pH/low pH bleaching stage which results in a substantial decrease in the usage of chlorine dioxide required to brighten wood pulp.

Background Art

As is well known in the wood pulp bleaching art, the main objectives of wood pulp bleaching are to increase the brightness of the pulp and to make it suitable for the manufacture of printing and tissue grade papers by removal or modification of some of the constituents of the unbleached pulp, including the lignin and its degradation products, resins, metal ions, non-cellulosic carbohydrate components, and various types of flecks. The bleaching of chemical wood pulp is normally carried out in multiple processing stages utilizing elemental chlorine, caustic soda, hypochlorites, oxygen, hydrogen peroxide, and chlorine dioxide. The number of stages

required in a particular bleaching process is dependant upon the nature of the unbleached pulp as well as the end use to which the pulp will be put. A sulfate or kraft pulp is today most typically bleached in a five stage sequence which is designated as (CD)(EO)DED. In the (CD)(EO)DED designation, D denotes chlorine dioxide, C denotes elemental chlorine, E denotes caustic extraction, and O denotes oxygen gas. The multi-stage process in essence comprises a chlorination step (CD), a first oxidative extraction stage (EO), a first bleaching stage (D_1), a second caustic extraction stage (E_2), and a second and final bleaching stage (D_2).

In the conventional (CD)(EO)DED multi-stage bleaching process, each of the two chlorine dioxide bleaching stages is carried out in a one-step process at an end pH of about 3.8 for three hours at 70^o centigrade. It is commonly known that pH has an important bearing on brightness and strength properties as well as the chemical species present in the wood pulp mixture, and this particular pH has heretofore been considered optimal for each of the two chlorine dioxide bleaching stages in the (CD)(EO)DED sequence. It should also be appreciated that although the (CD)(EO)DED sequence has been specifically addressed, the one-step chlorine dioxide bleaching stage can be used in any D stage for most other

three, four, five, or six-stage bleaching processes known to those familiar with the art of wood pulp bleaching.

A shortcoming of the one-step chlorine dioxide bleaching stage presently used in the pulp and paper industry is that approximately 30% of the chlorine dioxide is lost to the formation of the unreactive species chlorite and chlorate, and this is very undesirable in view of the relatively high cost of chlorine dioxide. The present invention solves this well-known deficiency in state of the art chlorine dioxide bleaching by significantly reducing the chlorine dioxide loss during the chlorine dioxide bleaching process. The advantages of the reduced loss of chlorine dioxide are a very significant reduction in the cost of the wood pulp bleaching process as well as the reduction of pollution levels.

Disclosure of the Invention

In accordance with the present invention, applicant provides an improved process for bleaching wood pulp in an aqueous suspension using chlorine dioxide which substitutes a two-step bleaching stage for the conventional one-step bleaching stage known to those familiar with the wood pulp bleaching art. The novel process comprises first subjecting the aqueous wood pulp suspension to a first bleaching step by mixing it with an aqueous solution of chlorine dioxide and maintaining the

1st bleaching step ClO_2

mixture at a pH between about 5-10 for about 5-40 minutes. Next, an acid or acid gas is introduced into the mixture in order to bring the pH down to a pH between about 1.9-4.2, and the mixture is then subjected to a second bleaching step at the reduced pH for 2 or more hours, most suitably between about 2.5-3.9 hours. This novel process can be used in the D_1 or D_2 stage of the (CD)(EO)DED bleaching sequence as well as in any D bleaching stage of other three, four, five, six, and seven-stage bleaching sequences. The operating temperature during the novel process should be between about 55-85°C, and the pulp's final consistency should be between about 3-12%.

D) any bleaching stage

It is therefore an object of the present invention to provide more efficient chlorine dioxide bleaching in the wood pulp bleaching process.

It is another object of the present invention to significantly reduce the conversion of chlorine dioxide to non-bleaching chemicals during the wood pulp bleaching process.

It is still another object of the present invention to reduce the cost of the wood pulp bleaching process.

It is yet another object of the present invention to achieve a higher wood pulp brightness with a selected chlorine dioxide charge than has heretofore been possible.

Description of the Drawings

Some of the objects having been stated, other objects will become evident as the description proceeds, when taken in connection with the accompanying drawings, in which:

Figure 1 is a graph of the effect of pH on chlorate and chlorite formation in chlorine dioxide bleaching of kraft pulp (reprinted from "The Bleaching of Pulp", Ed. R. P. Singh, p. 137);

Figure 2 is a graph of D_1 brightness for the pulp of Figure 2 when the D_1 charge is varied on the pulp for the conventional one-step bleaching process and the novel two-step bleaching process of the present invention;

Figure 3 is a graph of D_2 brightness versus chlorine dioxide charge for the conventional one-step bleaching process and the novel two-step bleaching process of the present invention wherein the D_2 charge is 0.2% ClO_2 on pulp;

Figure 4 is a graph of D_1 and D_2 brightness versus chlorine dioxide charge for the conventional one-step bleaching process and the novel two-step bleaching process of the present invention;

Figure 5 is a graph of D_1 brightness versus percentage (%) chlorine dioxide on the pulp (D_1 charge)

for the conventional one-step bleaching process and the novel two-step bleaching process of the present invention;

Figure 6 is a graph of D_2 brightness for the pulp of Figure 5 when the D_2 charge is 0.2% chlorine dioxide on the pulp for the conventional one-step bleaching process and the novel two-step bleaching process of the present invention;

Figure 6(a) is a graph of final brightness versus ClO_2 charge for the conventional one-step process and the novel two-step bleaching process of the present invention using a (CD)(EO)D sequence. Reverted brightness is also shown after 24 hours at 105°C;

Figure 7 is a graph of D_1 viscosity versus D_1 pH for the conventional one-step bleaching process and high pH for the novel two-step bleaching process of the present invention;

Figure 8 is a graph of total organic chlorine (TOCl) or (AOX) in D_1 plus E_2 effluents versus chlorine dioxide charge in D_1 for the conventional one-step bleaching process and the novel two-step bleaching process of the present invention;

Figure 9 is a graph of chlorate formed in the D_1 stage versus end pH;

Figure 10 is a graph of chlorate formed versus D_1 charge and CE kappa number for conventional bleaching;

Figure 11 is a graph of chlorate formed versus D_1 charge and CE kappa number for the novel two-step high/low pH bleaching process of the present invention;

Figure 12 is a graph of chlorate formed as a percentage (%) of chlorine dioxide converted to chlorate versus percent (%) chlorine dioxide in D_1 for the conventional one-step bleaching process and the novel two-step high/low bleaching process of the present invention;

Figure 13 is a graph of D_1 pulp brightness versus the percentage of chlorine dioxide on the pulp (D_1 charge) for the conventional one-step bleaching process and the novel two-step high/low pH bleaching process of the present invention (wherein the middle line is the calculated brightness due to reduced chlorate formation);

Figure 14 is a graph of chlorate formation versus D_1 brightness for the conventional one-step bleaching process and the novel two-step high/low pH bleaching process of the present invention; and

Figure 15 is a schematic representation of two (2) different process systems for a wood pulp bleaching plant for incorporating the two-step high/low pH bleaching process of the present invention.

Best Mode for Carrying Out the Invention

Chlorine dioxide bleaching of kraft pulps is typically carried out at an end pH of 3.8 for 3 hours at 70° centigrade. It is commonly known that pH has an important bearing on brightness and strength properties as well as the chemical species present in the mixture. As shown in Figure 1 of the drawings, the formation of chlorate increases as the pH of the solution is decreased. Below pH 5 a major loss of oxidizing power occurs since the chlorate formed is inactive as a bleaching agent. Conversely, as the pH is increased, the conversion of chlorine dioxide to the chlorite anion is increased which is also inactive toward lignin. The sum of chlorite plus chlorate is lowest at end pH 3.8 which is found to be optimal for chlorine dioxide bleaching. However, formation of chlorite is not actually lost oxidizing capability since acidifying the chlorite solution forms chlorous acid which is known to be very reactive toward lignin.

In order to increase the efficiency of chlorine dioxide bleaching, a new two-step process has been discovered. The process is as follows:

1. Pulp is mixed with sodium hydroxide and subsequently mixed with chlorine dioxide in a conventional manner. The pH is maintained between about 6 and 7.5 for optimum brightness and viscosity although

pH 5-10
6-7.5
5-40 min
55-85°C

beneficial results are also found in a pH range of about 5-10. Reaction time is varied between about 5-40 minutes, and the reaction temperature is between about 55-85° centigrade, most suitably about 70° centigrade.

2. After the initial bleaching step, the pulp mixture is acidified to an optimum end pH of 3.8 with sulfuric acid, hydrochloric acid, or other suitable acid. Although a pH of 3.8 is optimal for brightness, end pH values of 1.9-4.2 have been recorded with substantial brightness gains over conventional bleaching methods. Final consistency of the pulp is between about 3-12%, most suitably about 10%, and reaction time in this second step is 2 or more hours, most suitably between about 2.5 and 3.9 hours. Reaction temperature is between about 55-85° centigrade, and most suitably about 70° centigrade.

150 - 234 min

To prove the efficacy of the new process generally described above, detailed bleaching experiments were carried out by applicant on southern pine kraft pulp. The furnish was obtained from the decker before the bleach plant, and to insure maximum mixing CD stage bleaching was done in plastic Nalgene bottles which rolled on a ball-mill type apparatus for the full reaction time. All other bleaching stages were carried out in sealed polyester bags which were kneaded at various times throughout the bleach to insure proper mixing.

Processing parameters used by applicants for the multiple bleaching stages are listed in Table 1 below. Chlorination stage charges were varied to achieve target (CD)E kappa numbers, and all charges are on OD brownstock pulp. Optimum high/low pH values are 6-7.5 and 3.8, respectively. Large batches of (CD)E pulp were made and then divided into individual DED runs for comparison. All comparisons were made on pulps from the same (CD)E batch, and all water used in bleaching and washing was distilled. Chlorine dioxide solutions used in testing were generated on site by acidifying sodium chlorite solution and absorbing the ClO_2 gas in cold distilled water. Chlorine content in the solutions was kept between 7 and 10% (active basis).

Processing parameters for the bleaching experiments and the analytical methods used in the experiments are as follows:

TABLE 1

Stage	Charge	Time	Temperature	Consistency	End pH
CD	.17-.22 x Kappa % Available Chlorine on Pulp (10% ClO_2 Substitution)	1 hour	30-40° C	3%	<1.8
E_1	0.7 x Cl_2 % Of Caustic on Pulp	1 hour	70° C	10%	>11.5
D_1	varied	3 hours	70° C	10%	3-4
H/L D_1	varied	5-15 mins. 2.75-2.9 hrs.	70° C 70° C	10.5-13% 10%	5-10 1-9-4.2
E_2	0.75%	1 hour	70° C	10%	>11.5
D_2	varied	3 hours	70° C	10%	3.5-3.8

BRIGHTNESS	Elrepho 2000 ISO
VISCOSITY	TAPPI T230 os-76
KAPPA NUMBER	TAPPI T236 hm-85
TOCl (AOX)	EPA method 9020
CHLORATE	Ion Chromatography

Brightness

On the basis of the results achieved in the bleaching tests, a substantial increase in brightness is always found using the high/low pH bleaching method as compared to conventional bleaching methods. As seen in Figure 2, the D_1 brightnesses achieved were higher than those of the present ClO_2 bleaching techniques. In Figure 2, high pH values are between 8 and 9.5, and low pH values are from 1.9-2.1. The control had end pH values of 3.3 to 3.7. At a brightness level of 76 ISO, a charge of 0.9% ClO_2 on OD pulp was needed for conventional bleaching while only 0.68% was needed using the high/low bleaching method. This accounts for a 24% savings in chlorine dioxide. In 5-stage (CD)(EO)DED bleaching, however, the effect of the brightness gain is reduced in the final bleaching stage (D_2). This is shown in Figure 3, where the pulps of Figure 2 are further bleached in the E_2 and D_2 stages wherein the D_2 stages are run conventionally. After the final bleaching stage, a 15% savings in chlorine dioxide is realized at a brightness of 88.3 ISO.

Regardless of the incoming (CD)E kappa number (lignin concentration), chlorine dioxide savings are always found using the high/low pH bleaching process. This is illustrated in Figure 4 for pulp with a (CD)E kappa number of 8.5. Again a savings of approximately 0.2% ClO_2 on pulp is realized in the D_1 stage, and the

magnitude of savings is lower at a comparable D_2 brightness. Thus, even at high (CD)E kappa values, substantial reductions in chlorine dioxide use are realized by the bleaching method of the invention.

Similar brightness ceilings are reached in the D_1 stage irrespective of which method of bleaching is used. This occurs around 84.0 ISO for both methods for an incoming (CD)E kappa of 4.4 (see Figure 5). In Figure 6, D_2 pulp from Figure 5 was found to have an 11% savings in chlorine dioxide even at a very high brightness of 90.5 ISO, but eventually the ceiling is reached at 91.4 ISO at a total charge of 1.2% ClO_2 on OD pulp.

One of the major applications of the novel high/low pH bleaching process is in a three stage sequence (see Figure 6(a)). Current trends toward reducing operational and capital costs of pulp mills have led to the development of short sequence technologies in the pulp and paper industry. The major three-stage sequences are (CD)(EO)D and (CD)(EOP)D, and with high/low pH bleaching it is possible to decrease chlorine dioxide usage by as much as 29% in these processes.

Pulp Viscosity

Pulp viscosity measurements were made using TAPPI standard T 230 os-76. Earlier experimental work has indicated that chlorine dioxide at a pH of less than 5 reacts selectively with lignin, and at a pH greater than

7 chlorine dioxide reacts with the carbohydrate and lignin in the pulp vigorously, which in turn degrades the cellulose chain. As shown in Figure 7, pulp viscosity depends heavily on the pH of the reacting mixture. Pulp viscosity decreases slowly from pH 6 to 7, then falls rapidly at pH values higher than 7. The decrease in viscosity at the high pH for the two-step high/low pH bleaching process is not significant because of the low reaction time in the high pH step. From viscosity and brightness data obtained, a pH of 6-7.5 and a pH of 3.8 is optimal for the high pH and low pH, respectively, in the two-step high/low pH bleaching process.

Table 2 below gives an example of pulp qualities measured from a bleach run performed on a pulp of (CD)E kappa = 4.4 and viscosity 25 cp. An average viscosity drop of 0.6 centipoise was detected for the two-step high/low pH bleaching process as compared to conventional bleaching results. Other bleach runs performed showed a similar effect.

TABLE 2

CONVENTIONAL BLEACHING

Charge	End pH	CED Bright ISO	(CD)EDED Bright ISO	Viscosity CP
0.4%	3.6	60.2	86.0	24.8
0.6%	3.4	70.5	89.2	24.7
0.8%	3.4	78.3	90.4	24.7
1.0%	3.5	84.6	91.4	24.5

HIGH/LOW pH BLEACHING

Charge	High pH	Low pH	CED Bright ISO	(CD)EDED Bright ISO	Viscosity CP
0.4%	7.2	3.8	67.5	87.6	24.5
0.6%	7.1	3.7	78.5	89.9	24.1
0.8%	6.7	3.2	82.2	90.9	24.0
1.0%	7.0	3.0	84.5	91.4	24.1

Total Organic Chlorine (TOCl) or (AOX)

TOCl (AOX) measurements in applicant's tests were made on both the D_1 and E_2 for one data set. The values were added together and are shown in Figure 8 of the drawings. Surprisingly, conventional bleaching TOCl values were parabolic versus an increasing ClO_2 charge while TOCl values with the high/low pH bleaching method varied only slightly. A greater decrease in TOCl from bleaching with the two-step high/low pH bleaching process can be realized by substituting the chlorine dioxide saved in the D_1 stage back into the chlorination stage (CD) of the multi-stage bleach sequence. This would result in a decrease in TOCl (AOX) in effluents from the bleach plant.

Chlorate

Chlorate (ClO_3^-) is a well known herbicide, and discharge of chlorate from paper mills has been gaining more attention from environmentalists now that possible detrimental effects on various microalgaes have been observed. Thus, improving the efficiency of chlorine dioxide bleaching by lowering chlorate production may

have a favorable impact on both economic and environmental issues. Conversion of chlorine dioxide to chlorate can be lowered by the two-stage high/low pH bleaching method for most chemical charges on pulp. At very high chemical charges (or lower lignin concentrations), chlorate formation is independent of whether the new or conventional bleaching method is used, because a brightness ceiling is reached.

Thus, it is important to determine if the chlorine dioxide saved using the two-step high/low pH bleaching process is due to a subsequent decrease in the formation of chlorate. The two possible pathways of forming chlorate are set forth in Equations 1 and 2 below:

Equation 1 $$2ClO_2 + 2OH^- \text{---->} ClO_3^- + ClO_2^- + H_2O$$

Equation 2 $$2HClO_2 \text{---->} H^+ + HClO + ClO_3^-$$

Equation 1 is not a very prominent reaction in bleaching carried out at pH 7 since only a small concentration of hydroxyl ions are present. Under typical bleaching conditions, the pH starts around 5 and drops to less than 4 by the end of the bleaching process. At pH 5, less than 1% hydroxyl ions would be present for reaction, and at pH 4 only 0.1% exist. Supporting evidence for this observation is shown in Figure 9 of the drawings. The trend indicated shows that as the pH is increased up to 9, the formation of chlorate decreases.

The major pathway for chlorate formation is Equation 2 above. In principle, chlorous acid reacts with itself to form chlorate and hypochlorous acid. This is a biomolecular reaction which is considered to be slow at low concentrations. Chlorous acid, as stated above, is very reactive toward lignin. Chlorous acid oxidizes lignin and is reduced to hypochlorous acid according to Equation 3:

Equation 3 $HClO_2$ + LIGNIN ---> HClO + OXIDIZED LIGNIN

During chlorine dioxide bleaching, a competitive pathway is present for consumption of chlorous acid. A high chemical charge would increase the rate of reaction of Equation 2, and a high lignin concentration would increase the rate of reaction of Equation 3. Figure 10 shows a plot of D_1 charge of chlorine dioxide versus % chlorine dioxide converted to chlorate for conventional chlorine dioxide bleaching. As the lignin concentration is increased (low chemical charge or higher kappa number) less chlorate is formed. Likewise if a high concentration of chemical is present (low kappa number), the higher the formation of chlorate. The same trend also holds true for the two-step high/low pH bleaching process as can be seen in Figure 11. From Figures 10 and 11, it is evident that the two-step high/low pH bleaching process significantly lowers chlorate formation at most chemical charges. However, little difference is seen at high charges where the brightness ceiling is reached.

Corresponding chlorate measurements for the brightness shown in Figure 5 are plotted on Figure 12. Again, as the charge is increased, the formation of chlorate rises. In order to determine the chlorine dioxide savings in terms of chlorate reduction, the chlorate measurements are expressed as available chlorine. At a brightness of 78.3 ISO, the high/low pH bleaching process and conventional bleaching required 0.6% and 0.8% ClO_2 on pulp, respectively. These charges correspond to 1753 parts per million (ppm) and 2338 ppm, respectively, as available chlorine. The difference provides a savings of 585 ppm available chlorine. Chlorate measurements were found to be 351 ppm and 423.3 ppm as available chlorine for the high/low pH bleaching process and normal bleaching, respectively, at a charge of 0.6% on pulp for a 17% reduction. Subtraction yields a savings of 72.3 ppm available chlorine, which corresponds to only 17% of the total savings realized of 423.3 ppm. Figure 13 of the drawings demonstrates this effect by replotting Figure 6 with the calculated savings due to chlorate reduction. It is apparent that a decrease of chlorate is not sufficient to explain the total ClO_2 savings. A change in lignin structure and/or greater solubilization of the lignin may be possible explanations for the total savings in the ClO_2 observed in the tests.

A larger reduction in chlorate is realized at a comparable D_1 brightness. As shown in Figure 14, it is possible to reduce chlorate by as much as 45% (at 78.3 ISO) using the two-step high/low pH bleaching process as compared to a conventional ClO_2 bleaching stage. Chlorate formation in the D_2 stage is identical for either bleaching process since they are carried out identically.

Process Apparatus

The two-step high/low pH bleaching process can be implemented in both a new plant or an existing pulp bleaching plant. The optimum design schematic is shown in Figure 15, where ClO_2 and caustic are added to the first mixer. The pulp flows into a J or U tube (Figure 15A) or upflow tower (Figure 15B) with a retention time of approximately 5-40 minutes. A second mixer is provided to mix the acid for pH adjustment of the wood pulp. The pulp can then be discharged directly to a downflow tower. The retention time in the downflow tower is 2 or more hours and most suitably between about 2.5-3.9 hours. In an existing bleach plant the simplest method for implementing the two-step high/low pH bleaching process technology would be to install a mixer on the discharge from the upflow leg of the tower to the downflow leg of the tower.

Typical chemical charges for conventional bleaching process and high/low pH bleaching process stages are listed in Table 3 below. The chlorine dioxide savings is 4 lb/ton, while the caustic and the acid charge increase by 3 lb/ton and 3.6 lb/ton, respectively.

TABLE 3

	Conventional Bleaching	High/Low pH Bleaching
Chlorination		
% Chlorine	4.10	4.10
% ClO_2	.46	.46
Extraction		
% Caustic	3.4	3.4
CE kappa	4.4	4.4
Chlorine Dioxide		
% ClO_2	0.8	0.6
% NaOH	0.55	0.7
% H_2SO_4		0.18
Brightness (ISO)	78.3	78.5

The following conclusions can be drawn about the novel 2-step high/low pH bleaching process described herein from the bleaching of mill southern pine kraft pulps:

1. The high/low pH bleaching process reduces chlorine dioxide usage by as much as 24% in the D_1 stage;

2. The formation of chlorinated organic material characterized by TOCl can be decreased by the use of the

high/low pH bleaching process if the ClO_2 saved is substituted into the CD stage;

3. The formation of chlorate is decreased by as much as 45% in the D_1 stage using the high/low pH bleaching process at a target D_1 brightness;

4. The high/low pH bleaching process can be easily implemented in either a new mill or an existing mill; and

5. The formation of chlorate at acidic bleaching conditions is due to the biomolecular reaction of chlorous acid with itself. Formation of chlorate can be reduced by lower bleach chemical charges or higher kappa number pulps.

It will be understood that various details of the invention may be changed without departing from the scope of the invention. Furthermore, the foregoing description is for the purpose of illustration only, and not for the purpose of limitation--the invention being defined by the claims.

Claims

What is claimed is:

1. A bleaching process for bleaching wood pulp in an aqueous suspension using chlorine dioxide, comprising the steps of:

subjecting said aqueous wood pulp suspension to a first bleaching step by mixing it with of chlorine dioxide and maintaining the mixture at a pH between about 5-10 for about 5-40 minutes;

decreasing the pH to a pH between about 1.9-4.2;

subjecting said mixture to a second bleaching step at the reduced pH for about 2 or more hours.

2. A bleaching process according to claim 1, wherein caustic is also mixed with said aqueous wood pulp suspension during said first bleaching step.

3. A bleaching process according to claim 2 wherein said caustic comprises sodium hydroxide.

4. A bleaching process according to claim 1 wherein the pH of the mixture during said first bleaching step is between about 6-7.5.

5. A bleaching process according to claim 1 wherein the temperature during said first bleaching step is between about 50-85° centigrade.

6. A bleaching process according to claim 5 wherein the temperature during said first bleaching step is about 70° centigrade.

7. A bleaching process according to claim 1 wherein the pH is decreased with an acid.

8. A bleaching process according to claim 1 wherein the pH of the mixture during said second bleaching step is about 3.8.

9. A bleaching process according to claim 1 wherein the temperature during said second bleaching step is between about 55-85° centigrade.

10. A bleaching process according to claim 9 wherein the temperature during said second bleaching step is about 70° centigrade.

11. A bleaching process according to claim 1 wherein the final consistency of the mixture after the second bleaching step is between about 3-12%.

12. A bleaching process according to claim 11 wherein the final consistency of the mixture after the second bleaching step is about 10%

13. A bleaching process according to claim 1 wherein said bleaching process is used in a three stage sequence process.

14. A bleaching process according to claim 1 wherein said bleaching process is used as the first bleaching stage in a five stage sequence process.

15. A bleaching process according to claim 14 wherein the five stage sequence process is a (CD)(EO)DED process and the first bleaching stage is followed by conventional extraction and bleaching stages.

16. A bleaching process for bleaching wood pulp in an aqueous suspension using chlorine dioxide, comprising the steps of:

subjecting said aqueous wood pulp suspension to a first bleaching step by mixing it with caustic and chlorine dioxide and maintaining the mixture at a pH between about 6-7.5 and a temperature of about 70° centigrade for about 5-40 minutes;

introducing an acid into said mixture so as to bring the pH down to about 3.8;

subjecting said mixture to a second bleaching step at a temperature of about 70° centigrade for 2.5-3.9 hours.

17. A bleaching process according to claim 16 wherein said caustic comprises sodium hydroxide.

18. A bleaching process according to claim 16 wherein said acid is selected from the group consisting of sulfuric acid and hydrochloric acid.

19. A bleaching process according to claim 16 wherein the final consistency of the mixture after the second bleaching step is about 10%.

20. A bleaching process according to claim 16 wherein said bleaching process is used in a three stage sequence process.

21. A bleaching process according to claim 16 wherein said bleaching process is used as the D_1 bleaching stage in a five stage sequence process.

22. A bleaching process according to claim 21 wherein the five stage sequence process is a (CD)(EO)DED process and the D_1 bleaching stage is followed by conventional extraction (E_2) and bleaching (D_2) stages.

AMENDED CLAIMS

[received by the International Bureau
on 28 March 1991 (28.03.91);
original claims 1,2,7,13-16,18, 20-22 cancelled;
original claims 3-5,8,9,11,17 and 19 amended; new claims 23
and 24 added; other claims unchanged (5 pages)]

1. (Cancel)

2. (Cancel)

3. A bleaching process according to claim 23 wherein said alkali comprises sodium hydroxide.

4. A bleaching process according to claim 23 wherein the end pH of the mixture during said first bleaching step is between about 6.0-7.5.

5. A bleaching process according to claim 23 wherein the temperature during said first bleaching step is between about 50-85^{o} centigrade.

6. A bleaching process according to claim 5 wherein the temperature during said first bleaching step is about 70° centigrade.

7. (Cancel)

8. A bleaching process according to claim 23 wherein the end pH of the mixture during said second bleaching step is about 3.8.

9. A bleaching process according to claim 23 wherein the temperature during said second bleaching step is between about $55-85^{\circ}$ centigrade.

10. A bleaching process according to claim 8 wherein the temperature during said second bleaching step is about 70° centigrade.

11. A bleaching process according to claim 23 wherein the final consistency of the mixture after the second bleaching step is between about 3-12%.

12. A bleaching process according to claim 11 wherein the final consistency of the mixture after the second bleaching step is about 10%.

13. (Cancel)

14. (Cancel)

15. (Cancel)

16. (Cancel)

17. A bleaching process according to claim 24 wherein said alkali comprises sodium hydroxide.

18. (Cancel)

19. A bleaching process according to claim 24 wherein the final consistency of the mixture after the second bleaching step is about 10%.

20. (Cancel)

21. (Cancel)

22. (Cancel)

23. A bleaching process for bleaching wood pulp in the D_1 and/or D_2 bleaching stage in an aqueous suspension using chlorine dioxide and providing high brightness and a high brightness ceiling, comprising the steps of:

subjecting said aqueous wood pulp suspension to a first bleaching step during the D_1 and/or D_2 bleaching stage by mixing it with alkali and 10% to 50% of the total chlorine dioxide charge for about 5-40 minutes so that the pH at the end of said first bleaching step is between about 6.0-12.0; and

adding the remaining portion of the total chlorine dioxide charge and subjecting said mixture to a second bleaching step during the D_1 and/or D_2 bleaching stage for about 2 or more hours so that the pH at the end of the second step is between about 1.9-4.2.

24. A bleaching process for bleaching wood pulp in the D_1 and/or D_2 bleaching stage in an aqueous suspension using chlorine dioxide providing high brightness and a high brightness ceiling, comprising the steps of:

subjecting said aqueous wood pulp suspension to a first bleaching step during the D_1 and/or D_2 bleaching stage by mixing it with alkali and 10% to 50% of the total chlorine dioxide charge for about 5-40 minutes at a temperature of about 70°

centigrade so that the pH at the end of said first bleaching step is between about 6.0-7.5; and

adding the remaining portion of the total chlorine dioxide charge and subjecting said mixture to a second bleaching step during the D_1 and/or D_2 bleaching stage at a temperature of about 70° centigrade for about 2.5-2.9 hours so that the pH at the end of the second step is about 3.8.

FIG. 1

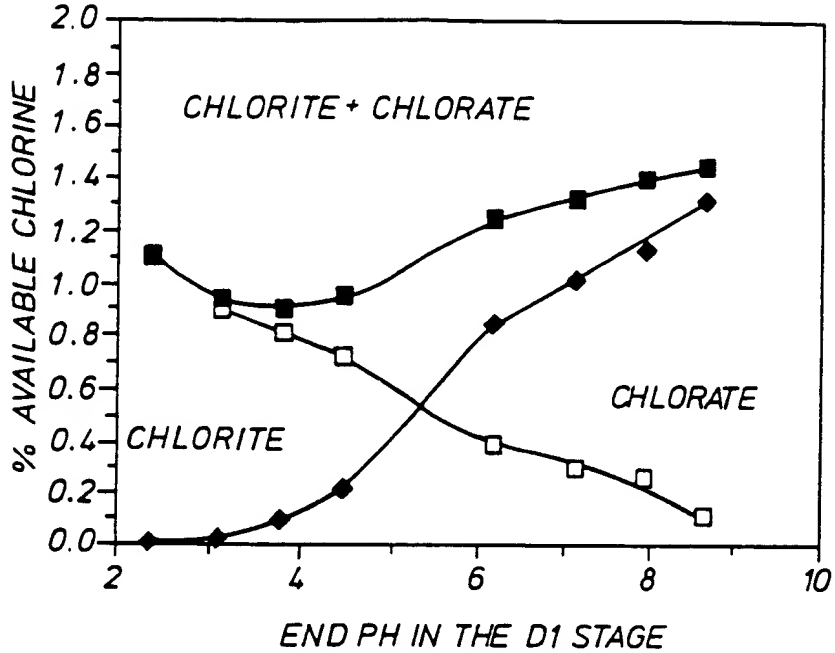

% AVAILABLE CHLORINE
CHLORITE + CHLORATE
CHLORITE
CHLORATE
END PH IN THE D1 STAGE

FIG. 2

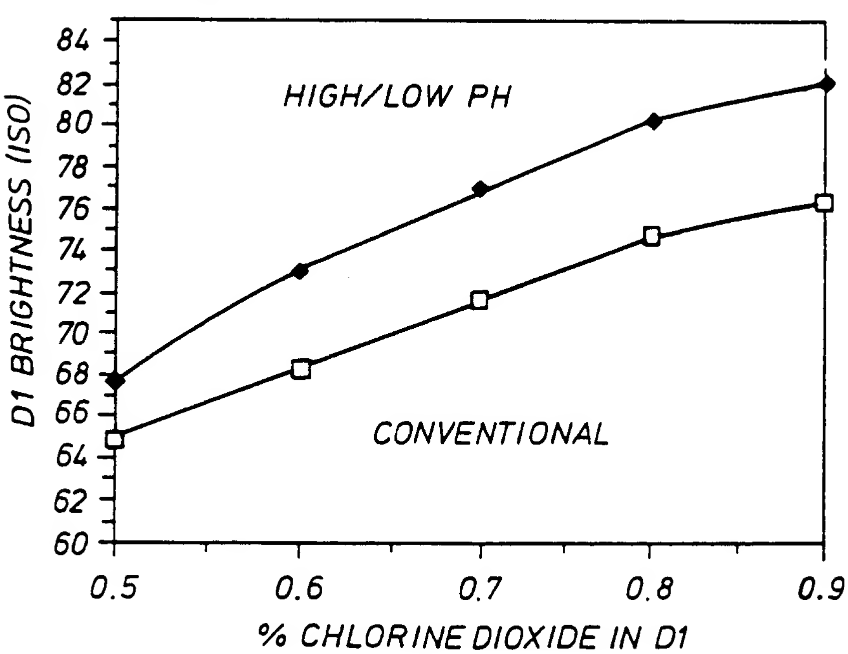

D1 BRIGHTNESS (ISO)
HIGH/LOW PH
CONVENTIONAL
% CHLORINE DIOXIDE IN D1

FIG.3

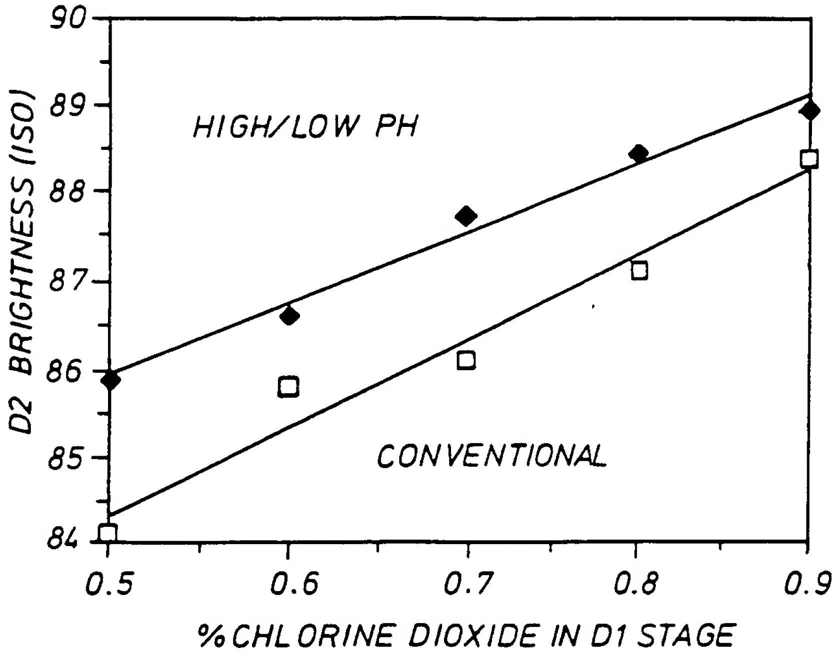

90
89
88
87
86
85
84
D2 BRIGHTNESS (ISO)
HIGH/LOW PH
CONVENTIONAL
0.5
0.6
0.7
0.8
0.9
% CHLORINE DIOXIDE IN D1 STAGE

FIG.4

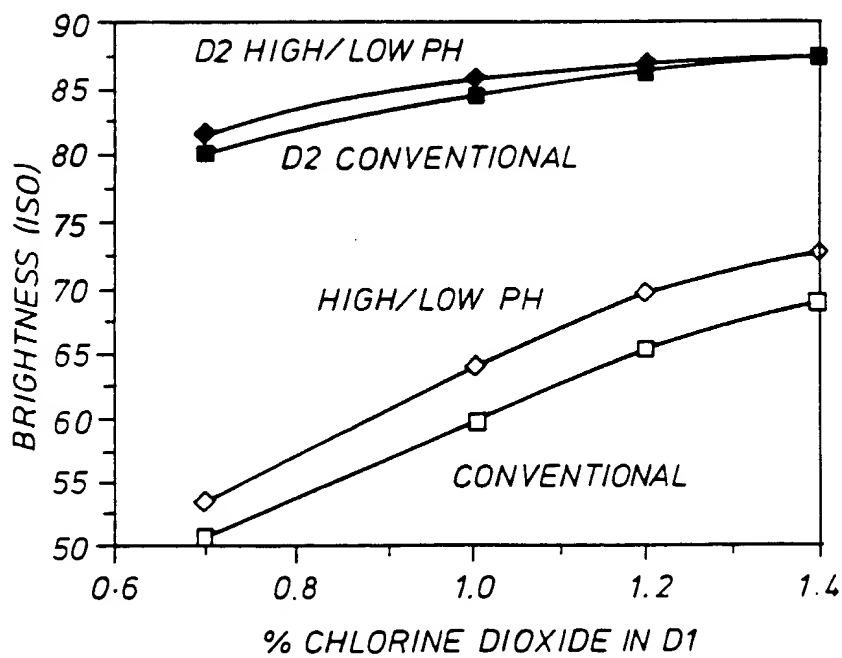

90
85
80
75
70
65
60
55
50
BRIGHTNESS (ISO)
D2 HIGH/LOW PH
D2 CONVENTIONAL
HIGH/LOW PH
CONVENTIONAL
0·6
0.8
1.0
1.2
1.4
% CHLORINE DIOXIDE IN D1

FIG.5

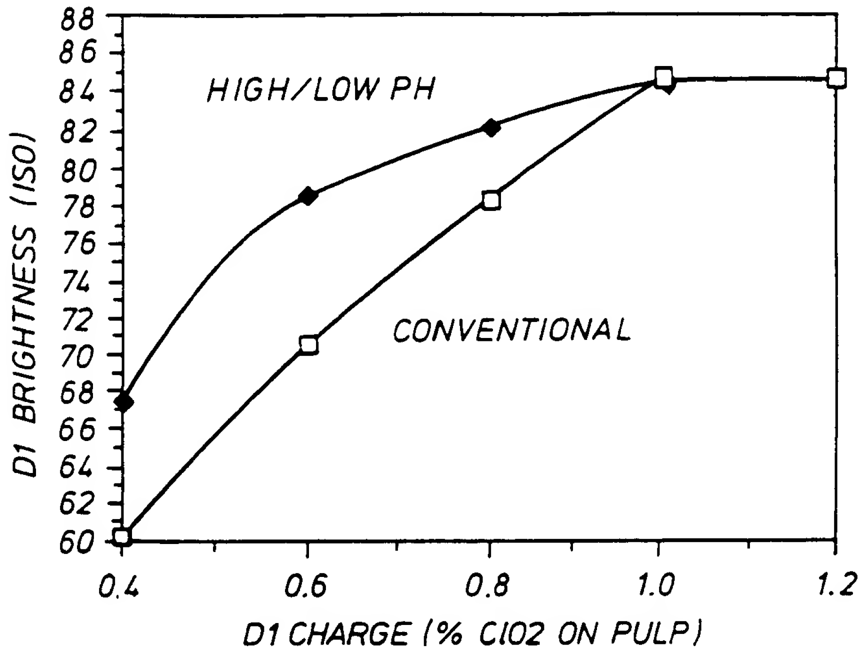
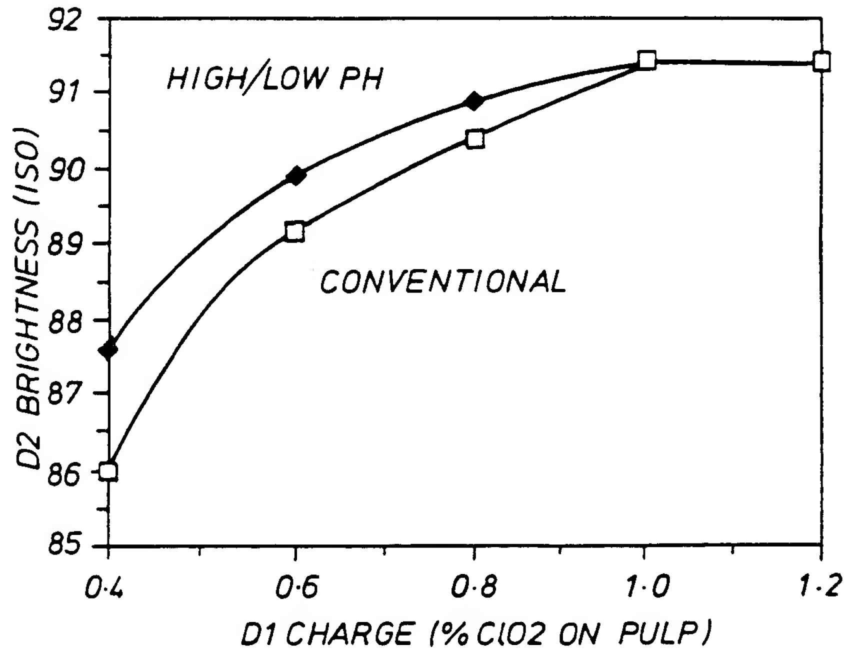
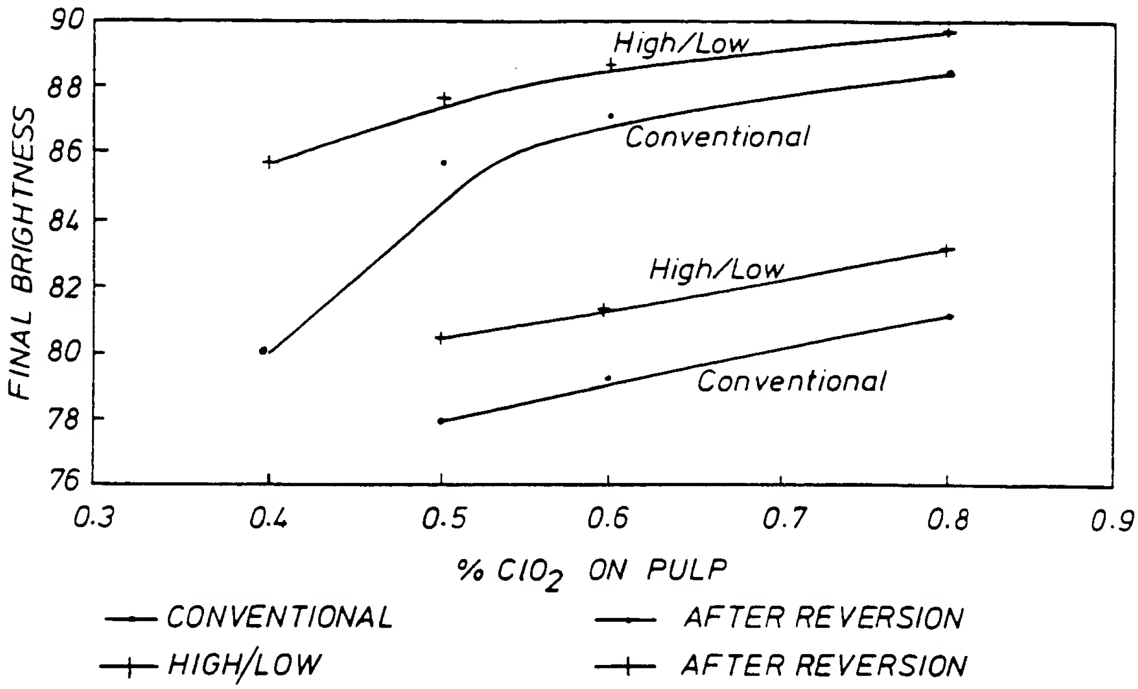

88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
D1 BRIGHTNESS (ISO)
HIGH/LOW PH
CONVENTIONAL
0.4
0.6
0.8
1.0
1.2
D1 CHARGE (% ClO2 ON PULP)

FIG.6


92
91
90
89
88
87
86
85
D2 BRIGHTNESS (ISO)
HIGH/LOW PH
CONVENTIONAL
0·4
0·6
0·8
1·0
1·2
D1 CHARGE (% ClO2 ON PULP)



(DC)(EO) Kappa = 2.7 FIG.6a

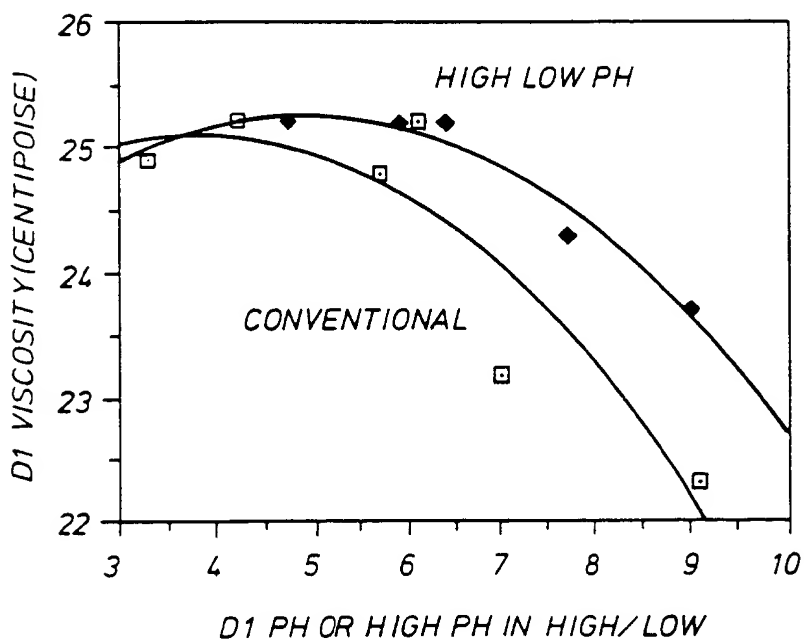


FIG.7

FIG.8

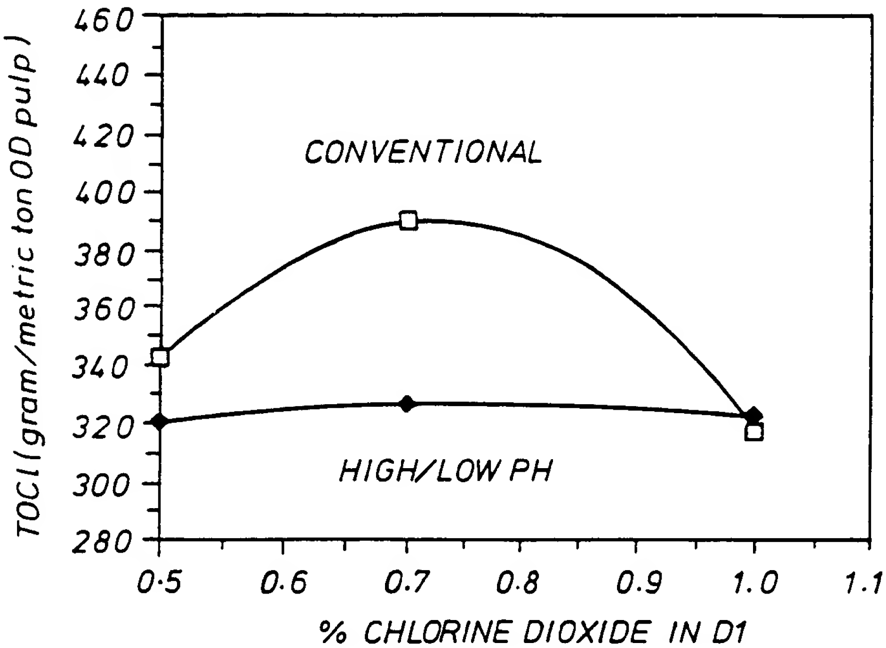

460
440
420
400
380
360
340
320
300
280
TOCl (gram/metric ton OD pulp)
CONVENTIONAL
HIGH/LOW PH
0·5
0·6
0·7
0·8
0·9
1.0
1.1
% CHLORINE DIOXIDE IN D1

FIG.9

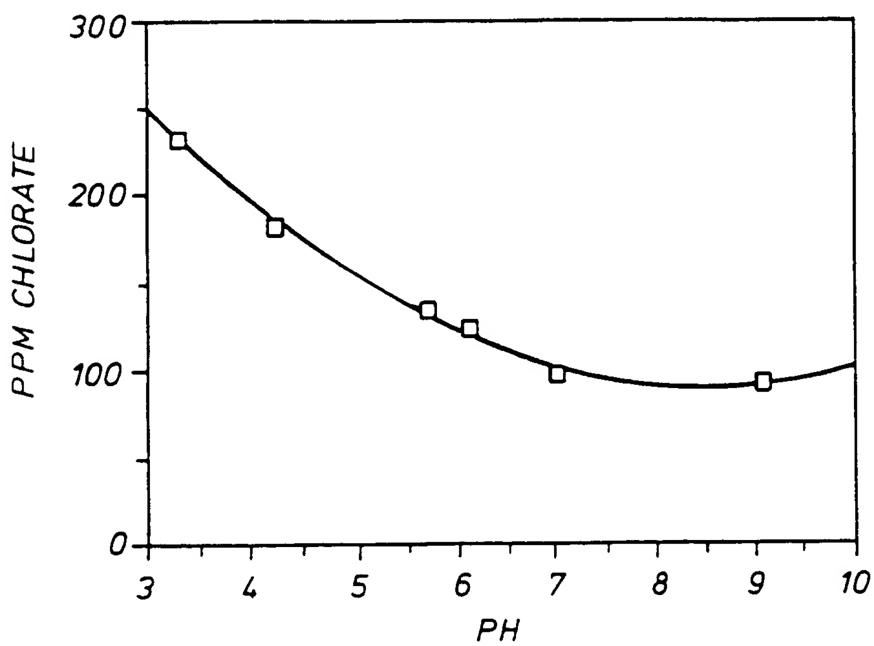

300
200
100
0
PPM CHLORATE
3
4
5
6
7
8
9
10
PH

FIG.10

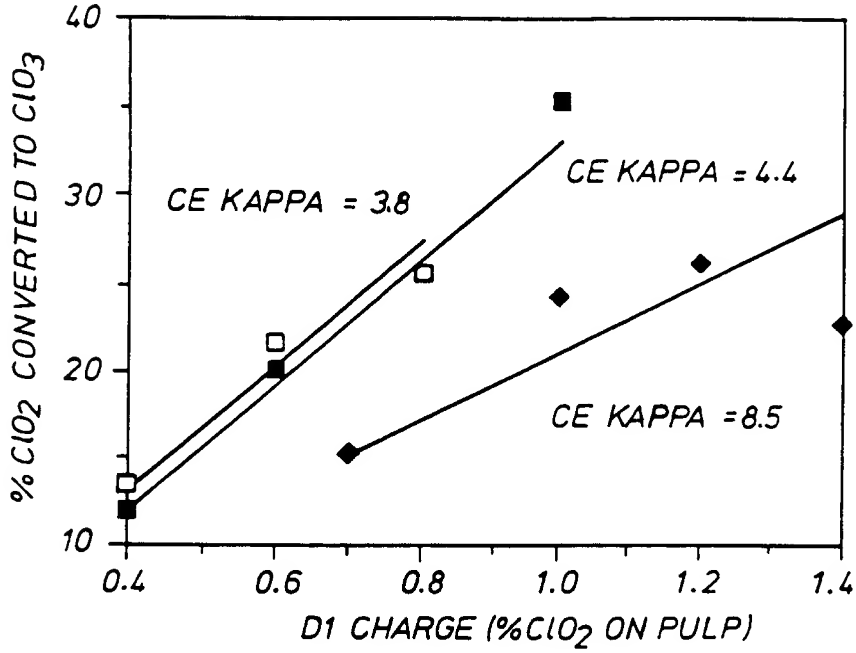

40
30
20
10
% ClO2 CONVERTED TO ClO3
CE KAPPA = 3.8
CE KAPPA = 4.4
CE KAPPA = 8.5
0.4
0.6
0.8
1.0
1.2
1.4
D1 CHARGE (%ClO2 ON PULP)

FIG.11

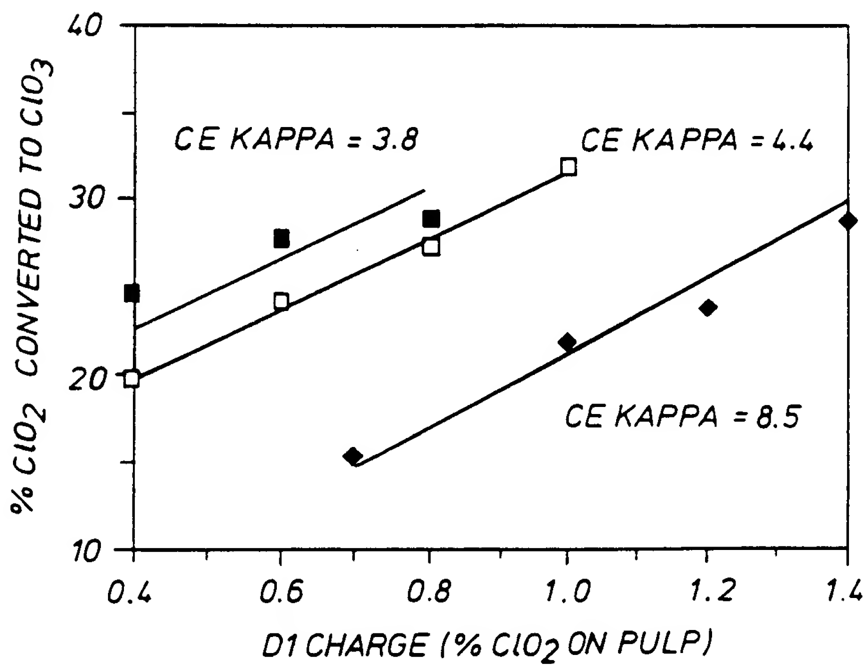

40
30
20
10
% ClO2 CONVERTED TO ClO3
CE KAPPA = 3.8
CE KAPPA = 4.4
CE KAPPA = 8.5
0.4
0.6
0.8
1.0
1.2
1.4
D1 CHARGE (% ClO2 ON PULP)

FIG.12

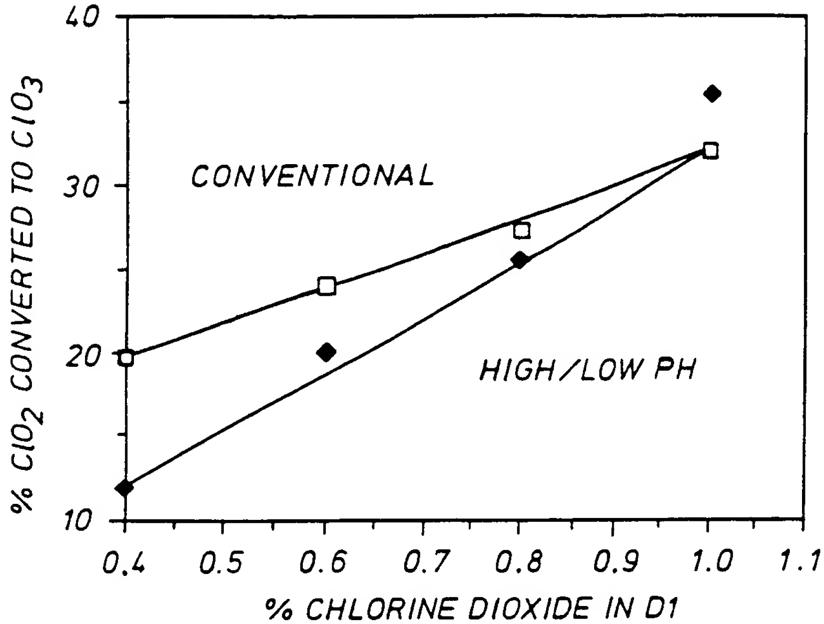

40
30
20
10
% ClO2 CONVERTED TO ClO3
CONVENTIONAL
HIGH/LOW PH
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
% CHLORINE DIOXIDE IN D1

FIG.13

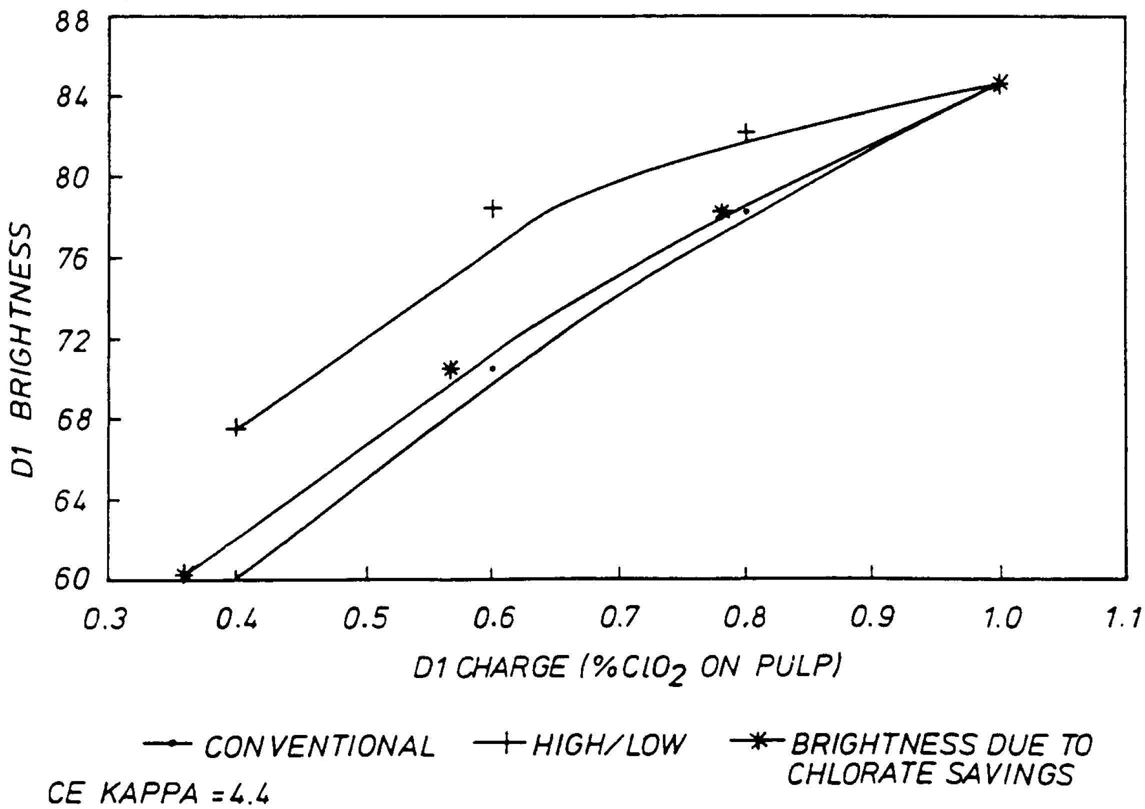
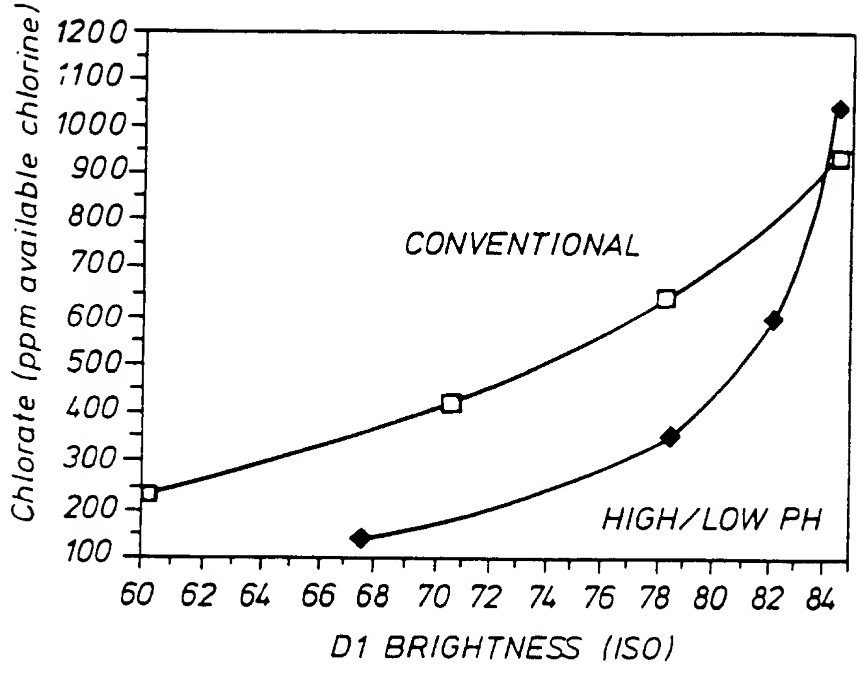

88
84
80
76
72
68
64
60
D1 BRIGHTNESS
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
D1 CHARGE (%ClO2 ON PULP)
CONVENTIONAL
HIGH/LOW
BRIGHTNESS DUE TO CHLORATE SAVINGS
CE KAPPA =4.4

FIG.14.


Chlorate (ppm available chlorine)
1200
1100
1000
900
800
700
600
500
400
300
200
100
CONVENTIONAL
HIGH/LOW PH
60 62 64 66 68 70 72 74 76 78 80 82 84
D1 BRIGHTNESS (ISO)

MILL APPLICATIONS

FIG.15 A

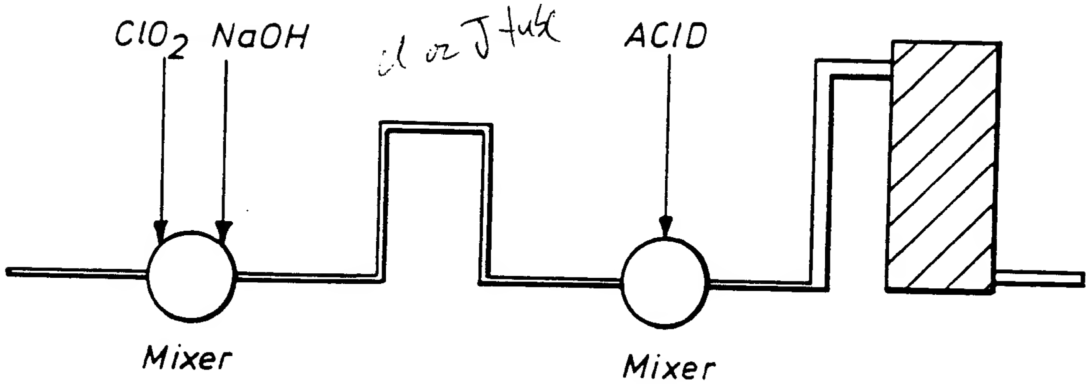
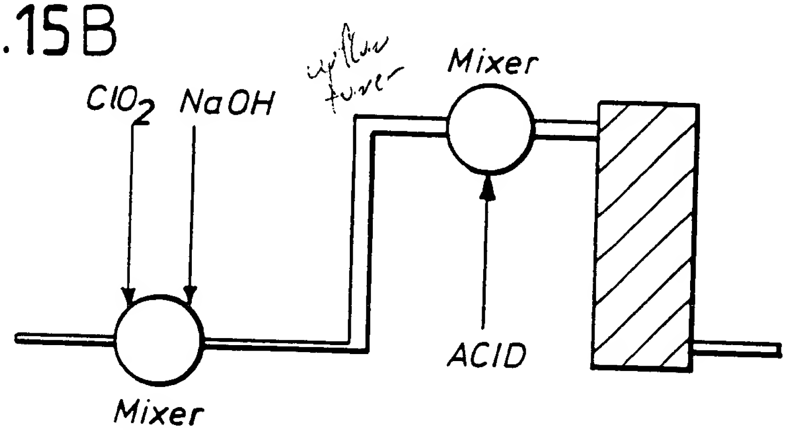


FIG.15B



INTERNATIONAL SEARCH REPORT

International Application No PCT/US90/05825

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5) : D21C 9/14,9/147
U.S. Cl : 162/65,66,67,87,88,89,90

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	162/65,89

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	US,A 3,433,702 (JACK ET AL) 18 March 1969 See Column 3, Lines 50-62.	1-14,16-21
X	US,A 4,274,912 (CARLES ET AL) 23 June 1981 See Column 1, Lines 65-68.	1-14,16-21
X	Pulp & Paper Canada (REEVE ET AL) December 1981 "The Effluent-Free Bleached Kraft Pulp Mill Part XII", See Figure 2.	1-14,16-21
X	Journal Pulp & Paper Science (MACAS ET AL) 03 May 1987 "The Effect of Chlorine in the D. Stage" Volume 13, No. 3, See Page J107.	1-14,16-21
	(con't)	

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
06 December 1990	07 FEB 1991
International Searching Authority [1]	**Signature of Authorized Officer [20]**
ISA/US	for STEVE ALVO Nguyen Ngoc-Ho NGUYEN NGOC-HO INTERNATIONAL DIVISION

Form PCT/ISA/210 (second sheet) (May 1986)

International Application No. PCT/US90/05825

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

X	TAPPI JOURNAL (ENZ ET AL) June 1984 "Oxidative Extraction: An Opportunity for Splitting the Bleach Plant". See Page 57.	15, 22

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers , because they relate to subject matter [1] not required to be searched by this Authority, namely:

2. ☐ Claim numbers .... , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [1], specifically:

3. ☐ Claim numbers__________, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.